

REMARKS

In response to the above Office Action, the claims have been amended to avoid the objection to the claims and the rejection of certain claims under 35 U.S.C. §112, second paragraph.

More specifically, claims 1 and 29 have been amended to replace "on" in the fourth line from the end of the claim with "part of."

Claim 7 has been amended to correct the spelling of "heterohydrocarbyl group."

Regarding claims 10 and 32, the various members of the Markush groups have been amended to correctly define them as divalent groups.

As the examiner points out, a "hydrocarbyl" group is a monovalent group, whereas B as a linking group is a divalent group. The proper nomenclature for such a group is "hydrocarbylene." See attached Exhibits A and B. Similar amendments have been made to 1,2-ethane, 1,2-propane, 1,2-catechol, and dimethylhydrazine to make them divalent groups.

Since it is clear from the teaching of the specification that B is a divalent group, it is not believed that these amendments to claims 10 and 32 or the conforming amendments to page 6 of the specification represent the addition of any new matter.

In addition in each claim, "and" has been replaced with "or."

Claims 17 and 37 have been amended as suggested by the Examiner.

In claim 25, the phrase "the transition metal from" has been deleted. Claim 26 has been cancelled and "further" added to claim 43.

Withdrawal of the rejection of the claims under §112, second paragraph is, therefore, requested.

In the Office Action the Examiner rejected claims 1-26 and 29-43 under 35 U.S.C. §102(b) for being anticipated by Sato et al. (JP 07215896), hereafter Sato. A complete English translation of the reference is included for the Examiner's consideration. Claims 29, 31, 32, 34-36 and 38-45 were also rejected under 35 U.S.C. §102(b) [sic 102(e)] for being anticipated by Dixon et al. (U.S. 2005/0119516).

In response, claim 1 has been amended to include

“ . . . and an activator selected from the group consisting of organoaluminium compounds, organoboron compounds, organic salts, inorganic acids and salts, wherein the organoaluminium compounds are selected from the group of compounds of the formula AlR_3 , where each R_3 is independently a C_1 - C_{12} alkyl or a halide, aluminoxanes and modified aluminoxanes”

Support for this amendment can be found on page 9, second paragraph of the specification and on page 15, last paragraph. In Sato the activator disclosed is organic aluminium-t-butoxide. The last paragraph on page 19 of the English translation describes that aluminum alkoxides are different from and superior to oxygen-containing aluminium compounds obtained from hydrolysis with water, i.e., aluminoxanes.

In order to further illustrate the significance of the difference in activators, applicants offer the following explanation:

Aluminoxanes are generally prepared by the controlled addition of water to an alkylaluminium compound, such as trimethylaluminium. In such process the alkylaluminium compounds are only partially hydrolyzed to prevent or at least to reduce the formation of aluminium hydroxide during the preparation of aluminoxanes. Commercially available aluminoxanes are sold and used in a diluted form (paraffinic or aromatic solutions containing, e.g., 7 mass % A) and such solutions consequently

include unreacted alkylaluminium. Structurally the aluminosiloxane molecules themselves can be represented by the general formula $(R^a\text{Al-O})_n$ and $R^b(R^c\text{-Al-O})_n\text{-AlR}^d_2$ wherein R^a , R^b , R^c , and R^d are independently a $C_1\text{-}C_{30}$ alkyl or halo-alkyl radical, for example, methyl, ethyl, butyl, 2-methyl-propyl, hexyl and octyl; and n has the value of 2 to 50. Preferably n is at least 4. In other words, the aluminosiloxane molecules are oligomers (with Al-O-Al bridges) of smaller subunits and thus contain more than one Al atom.

On the other hand, aluminium alkoxides such as aluminium-*t*-butoxide can easily be prepared in high yield by reacting an alkylaluminium compound, such as triethylaluminium, with an alcohol. for example, reacting triethylaluminium with *t*-butanol will lead to aluminium-*t*-butoxide ($\text{Al}(\text{O-}t\text{-Bu})_3$) and ethane. From Preparation Example 1 of the Sato reference it is clear that this is the activator species which was formed as “. . . agitation was continued until generation of gas stopped.” This means that no further ethane gas was produced and the reaction to aluminium-*t*-butoxide was completed. This is confirmed by the last paragraph of page 19 of the translation of Sato.

It should thus be clear that such an aluminium alkoxide molecule contains only a single monomeric unit and only one Al atom, but no Al-O-Al bridges are present. Furthermore, an aluminium alkoxide molecule (e.g., $\text{Al}(\text{OMe})_3$) does not contain any reactive Al-alkyl moieties (Al-methyl in this example), whereas the corresponding aluminosiloxane (methylaluminosiloxane) and alkylaluminium (AlMe_3) molecules do. Aluminium alkoxides are also stronger Lewis acids than their corresponding aluminosiloxanes and alkylaluminiums. All these differences ensure that the chemistry and reactivity of these three classes of compounds differ substantially.

With respect to claim 29, this has been limited to the subject matter of claim 31, and claim 31 has been cancelled. It is submitted that this ligand is not disclosed in either of Sato or Dixon.

Withdrawal of Sato and Dixon as a ground of rejection of independent claims 1 and 29 under §102 and claims 2-25 and 28 dependent from claim 1 and claims 32-45 dependent from claim 29 is, therefore, requested.

Finally, enclosed is a Terminal Disclaimer disclaiming the terminal portion of any patent to be granted on this application that would extend beyond the expiration date of any patent to be granted on Serial No. 10/539,237.


Entry of the above amendments and allowance of claims 1-25, 28, 29, and 32-45 is, therefore, requested. Applicants appreciate the Examiner's helpful advice in placing this case in condition for acceptance.

Please grant any extensions of time required to enter this response and charge any additional required fees to our Deposit Account 06-0916.

Respectfully submitted,

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Attachments: **Exhibits A and B (two pages)**
 English Translation of JP 07215896
 Terminal Disclaimer

hydrocarbyl groups

Univalent groups formed by removing a hydrogen atom from a *hydrocarbon*, e.g. ethyl, phenyl.

See *heterocyclyl, organoheteryl, organyl groups*.

1995, 67, 1341

hydrocarbylene groups

Divalent groups formed by removing two hydrogen atoms from a *hydrocarbon*, the free valencies of which are not engaged in a double bond, e.g. 1,3-phenylene, $-\text{CH}_2\text{CH}_2\text{CH}_2-$ propane-1,3-diyl, $-\text{CH}_2-$ methylene.

1995, 67, 1341

Translation of Jpn. Pat. Appln. KOKAI Publication No. 7-215896

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TITLE OF THE INVENTION

METHOD FOR MANUFACTURING α -OLEFIN OLIGOMER

[Abstract]

[Object]

As compared with the case where oxygen-containing aluminum compounds obtained through hydrolysis with water, and the like are applied, selectivity of trimer or tetramer of ethylene, hexene-1, or octene-1 which is useful as a comonomer for a linear low-density polyethylene (L-LDPE) can be improved by using an aluminum alkoxide as a cocatalyst.

[Constitution]

A method for manufacturing α -olefin oligomer using a catalyst composition consisting of a chromium compound, an

electron donor, and an aluminum alkoxide, wherein a compound obtained by reaction of an organic aluminum compound and an alcohol or an alkoxide is used particularly as the aluminum alkoxide.

CLAIMS

[Claim 1]

A method for manufacturing an α -olefin oligomer, characterized by using a catalyst composition consisting of a chromium compound, an electron donor, and an aluminum alkoxide.

[Claim 2]

The method for manufacturing an α -olefin oligomer according to claim 1, characterized by using a compound obtained by reaction of an organic aluminum compound and an alcohol or an alkoxide as the aluminum alkoxide.

[Claim 3]

The method for manufacturing an α -olefin oligomer according to claim 2, characterized by using a secondary or tertiary alcohol or alkoxide as the alcohol or alkoxide.

[Claim 4]

The method for manufacturing an α -olefin oligomer according to any one of claims 1 to 3, characterized by using, as the aluminum alkoxide, a reaction product obtained by subjecting a trialkyl aluminum to alcoholysis with an alcohol.

[Claim 5]

The method for manufacturing an α -olefin oligomer according to any one of claims 1 to 4, characterized by using the aluminum alkoxide in a molar ratio of 1 to 10000 with respect

to the chromium compound.

[Claim 6]

The method for manufacturing an α -olefin oligomer according to any one of claims 1 to 5, characterized by further using a catalyst composition containing a reducing agent.

[Claim 7]

The method for manufacturing an α -olefin oligomer according to any one of claims 1 to 6, characterized in that the reducing agent is an organic aluminum compound.

[Claim 8]

The method for manufacturing an α -olefin oligomer according to any one of claims 1 to 7, characterized in that the chromium compound is a compound of trivalent to hexavalent chromium having an oxygen anion as a ligand.

[Claim 9]

The method for manufacturing an α -olefin oligomer according to any one of claims 1 to 8, characterized in that the electron donor is an ether or amine.

[Claim 10]

The method for manufacturing an α -olefin oligomer according to any one of claims 1 to 9, characterized in that the electron donor is selected from the group consisting of tetrahydrofuran, dimethoxyethane, 2,3-dihydrofuran, and 3,4-dihydro-2H-pyran.

[Claim 11]

The method for manufacturing an α -olefin oligomer according to any one of claims 1 to 10, characterized by using

the electron donor in a molar ratio of 0.1 to 10000 with respect to the chromium compound.

DETAILED DESCRIPTION OF THE INVENTION

[0001]

[Field of Industrial Use]

The present invention relates to a method for manufacturing an α -olefin oligomer, and more particularly to a method for manufacturing an α -olefin oligomer by which hexene-1 and octene-1 particularly useful as a comonomer for linear low-density polyethylene (L-LDPE) can be selectively and efficiently manufactured.

[0002]

[Prior Art]

In recent years, it has been known that α -olefins having 4 to 12 carbon atoms, particularly hexene-1, octene-1 and the like are useful compounds as a comonomer for linear low-density polyethylene (L-LDPE), and that these α -olefins can be manufactured by oligomerization of ethylene and the like. Industrial oligomerization technology includes an oligomer manufacturing technique according to Schultz-Flory rule and another oligomer manufacturing technique represented by Poisson distribution. In the former technique, a molecular weight distribution of oligomer is indicated by α -value. In this respect, formation of butene-1 in a large amount is observed in the case where an α -value is 0.5, while formation of high-molecular weight α -olefins having 10 or more carbon atoms in a large amount is observed in the case where an α -value is

0.7, so that a comonomer for L-LDPE cannot be selectively manufactured. On the other hand, in the latter technique, α -olefins having 6 or 8 carbon atoms can be comparatively selectively manufactured. However, when the oligomer manufacturing technology, a so-called improved Ethyl method employed by Ethyl Corporation is analyzed in detail, it is found that the method entails complicated processes such as recycling of the produced olefin having 4 carbon atoms, dividing the reaction process into two steps, i.e., an alkylation step and a substitution step, requiring stoichiometrical use of a catalyst. Namely, the oligomerization of ethylene, particularly trimerization technology covered herein has been known from a long time ago. However, the technology has many problems that production of polymers cannot be suppressed, and increase in activity cannot be realized without using a solid catalyst together, for applying it as oligomer manufacturing technology.

[0003]

In the oligomer manufacturing technology as described above, a trimerization catalyst for ethylene, in which chromium element is used as oligomerization catalyst for olefins, has been heretofore known. However, in the case of a chromium carboxylate-based catalyst disclosed in, for example, Jpn. Pat. Appln. KOKOKU Publication No. 4-66457, only hexene-1 is produced as an oligomer, and in addition, the catalytic activity thereof is low. Furthermore, although a chromium pyrrolide-based catalyst disclosed in Jpn. Pat. Appln. KOKAI Publication No. 3-115406 can reduce formation of polymers to several % or less,

there is a problem of a slow reaction rate. In order to realize increase in such reaction rate, use of a solid acid is required. However, when a solid acid insoluble in a hydrocarbon solvent is used for the reaction, a filtration processing step must be added for the aftertreatment of the reaction, besides process constitutions such as a preparation of the solid acid, an addition of the powder, and the like are difficult.

[0004]

[Object of the Invention]

Under the circumstances, the present invention has been made for achieving an object of providing an industrially advantageous method for manufacturing an α -olefin oligomer, by which α -olefin oligomer, particularly hexene-1 and octene-1 useful as a comonomer for linear low density polyethylene (L-LDPE) can be selectively and efficiently manufactured through oligomerization of olefins, particularly ethylene.

[0005]

[Means for Achieving the Object]

Therefore, the present invention provides the following:

- (1) a method for manufacturing an α -olefin oligomer, characterized by using a catalyst composition consisting of a chromium compound, an electron donor, and an aluminum alkoxide;
- (2) the method for manufacturing an α -olefin oligomer according to (1), characterized by using a compound obtained by reaction of an organic aluminum compound and an alcohol or an alkoxide as the aluminum alkoxide;
- (3) the method for manufacturing an α -olefin oligomer according to (2), characterized by using a

secondary or tertiary alcohol or alkoxide as the alcohol or alkoxide; (4) the method for manufacturing an α -olefin oligomer according to any one of (1) to (3), characterized by using, as the aluminum alkoxide, a reaction product obtained by subjecting a trialkyl aluminum to alcoholysis with an alcohol; (5) the method for manufacturing an α -olefin oligomer according to any one of (1) to (4), characterized by using an aluminum alkoxide in a molar ratio of 1 to 10000 with respect to the chromium compound; (6) the method for manufacturing an α -olefin oligomer according to any one of (1) to (5), characterized by further using a catalyst composition containing a reducing agent; (7) the method for manufacturing an α -olefin oligomer according to any one of (1) to (6), characterized in that the reducing agent is an organic aluminum compound; (8) the method for manufacturing an α -olefin oligomer according to any one of (1) to (7), characterized in that the chromium compound is a compound of trivalent to hexavalent chromium having an oxygen anion as a ligand; (9) the method for manufacturing an α -olefin oligomer according to any one of (1) to (8), characterized in that the electron donor is an ether or amine; (10) the method for manufacturing an α -olefin oligomer according to any one of (1) to (9), characterized in that the electron donor is selected from the group consisting of tetrahydrofuran, dimethoxyethane, 2, 3-dihydrofuran, and 3,4-dihydro-2H-pyran; and (11) the method for manufacturing an α -olefin oligomer according to any one of (1) to (10), characterized by using the electron donor in a molar ratio of 0.1 to 10000 with respect to the chromium compound.

[0006]

The present invention will be described in more detail below. As the chromium compound constituting a catalyst composition used in the manufacturing method according to the present invention, use is made of chromium compounds in which the oxidation state of chromium is null-valent to hexavalent, preferably compounds of divalent to hexavalent chromium having an oxygen anion as a ligand, and more preferably compounds of trivalent or tetravalent chromium. Although these chromium compounds are not specifically limited, examples thereof include: carboxylates such as chromium (3) tris(2-ethylhexanoate), and chromium (3) tris(cyclohexylcarboxylate); chelate salts of β -diketone such as trisacetylacetonato chromium, and tris(2,2,6,6-tetramethyl-3,5-heptandionato) chromium; and alcoholates such as chromium (4) tetraethoxide, and chromium (4) tetra-t-butoxide. These chromium compounds may be used singly or in a combination of two or more of them.

[0007]

Moreover, an electron donor is used in the catalyst composition applied in the manufacturing method of the present invention. Any material which can donate an electron to the chromium center may be used as such electron donor. Examples of the electron donor include: cyclic ethers such as tetrahydrofuran, pyran, and dioxane; chain ethers such as dimethoxyethane, diethylene glycol dimethyl ether, and triethylene glycol dimethyl ether; cyclic vinyl ethers such as

2,3-dihydrofuran, and 3,4-dihydro-2H-pyran; chain vinyl ethers such as methyl vinyl ether, and ethyl vinyl ether; cyclic allyl ethers such as 2,5-dihydrofuran, and 5,6-dihydro-2H-pyran; chain allyl ethers such as methyl allyl ether, and ethyl allyl ether; aliphatic amines such as triethyl amine, and triethylene diamine; aromatic amines such as pyridine, and picoline; and heterocyclic compounds such as 2-oxazoline, and 6H-1,2,4-oxadiazine. Particularly, tetrahydrofuran, dimethoxyethane, 2,3-dihydrofuran, 3,4-dihydro-2H-pyran and the like are preferably used. These electron donors may be used singly or in a combination of two or more of them.

[0008]

Furthermore, an aluminum alkoxide is used in the catalyst composition applied in the manufacturing method of the present invention. As the aluminum alkoxide, organic aluminum alkoxides are preferably used, and moreover, compounds containing one to three alkoxides with respect to an aluminum atom, and particularly compounds obtained by reaction of an organic aluminum compound and an alcohol or an alkoxide are preferably used. Examples of the aluminum alkoxides include: reaction products obtained by subjecting trialkyl aluminum such as trimethyl aluminum, triethyl aluminum, and isobutyl aluminum to alcoholysis with an alcohol; reaction products of hydrides such as dibutyl aluminum hydride, and diethyl aluminum hydride and an alcohol; and aluminum alkoxides obtained by reaction of diethyl aluminum chloride or dibutyl aluminum chloride and a metal alcoholate. As the alcohols used for the preparation of

the above-described aluminum alkoxides, secondary or tertiary alcohols are used preferably. In this respect, there is such a tendency that a progress of the reaction of ethylene is slightly inferior in an aluminum alkoxide prepared from a primary alcohol such as n-butanol. Furthermore, a metal alcoholate of a secondary or tertiary alcohol is preferably used as the metal alcoholate. As metals constituting the metal alcoholates, metals belonging to Group 1 of the periodic table, such as lithium, sodium, and potassium are preferable. The above-described aluminum alkoxides may be used singly or in a combination of two or more of them.

[0009]

In the manufacturing method of the present invention, it is particularly preferred to use a reducing agent in the case where compounds of trivalent or tetravalent chromium are used according to needs. The reducing agent may be a material which can reduce the above-described chromium compounds. Preferred examples thereof include: organic aluminum such as trimethylaluminum, triethylaluminum, and triisobutylaluminum; organic zinc such as dimethyl zinc, diethyl zinc, and dibutyl zinc; hydrides such as lithium aluminumhydride, sodium borohydride, diethylaluminumhydride, dibutylaluminumhydride, sodium hydride, and lithium hydride; metals such as lithium, sodium, potassium, magnesium, and aluminum; and further, inorganic or organic compounds having the action to reduce trivalent to hexavalent chromium compounds. Organic aluminum such as trimethylaluminum, triethylaluminum, and

triisobutylaluminum are particularly preferably used.

[0010]

A blending amount of each component in the catalyst composition used in the manufacturing method of the present invention depends on a type of the chromium compound used. Generally, in the case of the aluminum alkoxide, it is within a range of 1 to 10000, preferably 10 to 5000, and more preferably 20 to 1000 in molar ratio with respect to the chromium compound. When the molar ratio is less than 1, the oligomer activity becomes low, while production of polymers becomes remarkable in the case where the molar ratio exceeds 10000. Moreover, the electron donor is used within a range of 0.1 to 10000, preferably 1 to 5000, and more preferably 2 to 2000 in molar ratio with respect to the chromium compound. In this case, when the molar ratio is less than 0.1, the production of polymers becomes dominant, while when the molar ratio exceeds 10000, the oligomer activity decreases. Furthermore, the reducing agent is used within a range of 0 to 10000, preferably 1 to 5000, and more preferably 1 to 2000 in molar ratio with respect to the chromium compound. In this case, an amount sufficient for reducing the raw material chromium compound to a divalent state is used as a quantity of the reducing agent, and the quantity is suitably determined depending on a type of the reducing agent.

[0011]

The catalyst composition used in the manufacturing method of the present invention may be prepared in accordance with a variety of methods. Specifically, the catalyst composition is

obtained by adding the aluminum alkoxide (obtained by subjecting an organic aluminum compound to alcoholysis with an alcohol) to a mixed solution of, for example, the chromium compound and an electron donor. Preferably, the preparation may be conducted in such a manner that an organic aluminum compound having reducing power is added to a mixed solution of, for example, a (trivalent to hexavalent) chromium compound and the electron donor to obtain a chromium complex in which the valency of chromium is reduced to divalent, or that the aluminum alkoxide is added after the reduced chromium complex is obtained. Moreover, the electron donor plays an important role in reducing the chromium compound in the preparation of the catalyst composition. Accordingly, the amount of the electron donor can be adjusted to be an amount optimal for the oligomerization reaction by appropriately distilling off a part thereof. The olefin used in the method for manufacturing an α -olefin oligomer is an α -olefin. Examples thereof include ethylene, propylene, butene-1, isobutylene, pentene-1, hexene-1, heptene-1, a variety of octenes, and mixtures thereof. Among them, ethylene is particularly preferred. In the above-described polymerization of olefins, an inert solvent is usually employed. Examples of such inert solvents include: aliphatic hydrocarbons such as pentane, hexane, heptane, and octane; alicyclic hydrocarbons such as cyclopentane, cyclohexane, and methylcyclohexane; and aromatic hydrocarbons such as benzene, toluene, xylene, and ethylbenzene. These solvents may be used singly, or in a combination of two or more of them.

[0012]

Furthermore, a reaction temperature is generally selected within a range of -10 to 200°C , and preferably 20 to 150°C . In the present invention, the optimum reaction temperature differs depending on a type of the electron donor used. For instance, when the above-described ethers such as dimethoxyethane, tetrahydrofuran, and dioxane are used as electron donors, a reaction temperature of 50 to 150°C , and further 80 to 130°C is preferred. When the above-described cyclic or chain vinyl ethers are used as electron donors, a reaction temperature of -10 to 100°C , and further 20 to 80°C is preferred. A reaction pressure is generally selected within a range of the atmospheric pressure to 200 kg/cm^2 , and preferably 5 to 100 kg/cm^2 . Although the above-described higher pressure can accelerate the reaction, there is a case where it becomes difficult to control the temperature of the reaction, when the pressure exceeds 200 kg/cm^2 . Moreover, a feed amount of the catalyst is selected such that a chromium concentration is in the range of 10^{-3} to 50 millimole/liter, preferably in the range of 10^{-2} to 5 millimole/liter. In the manufacturing method of the present invention, it is preferred to conduct the reaction under the conditions that the preferred conditions mentioned above in detail in the respective constitutions of the chromium compound, the electron donor, the aluminum alkoxide, and further the reducing agent are established. The manufacturing method of the present invention is preferably applied to producing simultaneously hexene-1 with octene-1 by using ethylene as the

raw material. Namely, when the manufacturing conditions of the catalyst and the reaction conditions are suitably selected, hexene-1 and octene-1 useful for a comonomer of linear low-density polyethylene can be selectively and efficiently manufactured.

[0013]

[Examples]

The present invention will be more specifically described in conjunction with Examples, but it should be noted that the invention is not restricted by these Examples.

Preparation Example 1 [Organic aluminum-t-butoxide]

A Schlenk flask having 300 milliliter inner volume was charged with 8.6 g (0.126 millimole) of t-butanol and cyclohexane to obtain 108 milliliter of a solution. To this solution, a cyclohexane solution of triisobutyl aluminum (TIBA) (1.0 mole/liter) was added dropwise and agitation was continued until generation of a gas stopped. The cyclohexane solution of aluminum-t-butoxide thus prepared contained 0.46 mole/liter amount of aluminum.

[0014]

Preparation Example 2 [Organic aluminum adamantoxide]

The organic aluminum adamantoxide was prepared in the same manner as in Preparation Example 1 except that adamantanol (0.126 millimole) was used in place of 8.6 g (0.126 millimole) of t-butanol. The cyclohexane solution of aluminum adamantoxide thus prepared contained 0.46 mole/liter amount of aluminum.

Preparation Example 3 [Organic aluminum bornoxide]

The organic aluminum bornoxide was prepared in the same manner as in Preparation Example 1 except that borneol (0.126 millimole) was used in place of 8.6 g (0.126 millimole) of t-butanol. The cyclohexane solution of aluminum bornoxide thus prepared contained 0.46 mole/liter amount of aluminum.

[0015]

Example 1

0.481 g (1 millimole) of chromium [valency: 3] 2-ethylhexanate was weighed into a Schlenk flask, and cyclohexane was added such that the total amount became 100 milliliter to dissolve chromium. The chromium solution was dark green, and the chromium concentration was 10 millimole/liter. Then, 0.90 g (10 millimole) of 1,2-dimethoxyethane was weighed in the Schlenk flask, and cyclohexane was added to obtain the total amount of 200 milliliter. An electron donor concentration of the solution was 50 millimole/liter. Twenty milliliter of the above-described dimethoxyethane solution (1 millimole of the electron donor) was added to 2.5 milliliter of the above-described chromium solution (Cr: 25 micromole), and the resulting solution was agitated for 5 minutes. To the solution, 20 milliliter of the organic aluminum-t-butoxide solution prepared in Preparation Example 1 (Al: 9.2 millimole) and 1.5 milliliter (1.5 millimole) of a cyclohexane solution of 1 mole/liter of TIBA were added. In order to obtain the total amount of 50 milliliter of a catalyst solution, 6 milliliter of cyclohexane was further added to the above-described solution, and the resulting solution was agitated for 30 minutes. The

catalyst solution was changed in color from green (chromium valency: 3) to ochre (chromium valency: 2) as a result of reduction treatment. Then, the catalyst solution prepared as described above was placed in an autoclave which had been sufficiently deaerated and dried, and had 200 milliliter inner volume. The contents of the autoclave were agitated at 200 rpm, and a temperature thereof was raised up to 100°C. Ethylene gas was fed to the contents while keeping the reaction temperature at 100°C, whereby the hold pressure was 35 Kg/cm² (gauge pressure). After the elapse of 23 minutes of the reaction time, the product was cooled, and the pressure was released. After filtering polymers off from the reaction solution, the products were analyzed by gas chromatography. As a result, the total amount of the ethylene reaction products was 3.14 g, a yield of hexene-1 was 2.64 g. Selectivities of the products were 84% by weight of hexene-1, 3% by weight of octene-1, 11% by weight of the polymers, and the remainder olefins having 10 or more carbon atoms.

[0016]

Example 2

A catalyst was prepared in the same manner as in Example 1 except that the organic aluminum adamantoxide prepared in the Preparation Example 2 was used in place of the organic aluminum-t-butoxide prepared in Preparation Example 1, and the reaction was conducted. The reaction was stopped at the point at which the reacted amount of ethylene corresponded to 1/3 of the amount in Example 1 (the reaction time was 214 minutes), and the products were analyzed. The total yield was 0.93 g and

the selectivity of hexene-1 was 47% by weight.

[0017]

Example 3

A catalyst was prepared in the same manner as in Example 1 except that the organic aluminum bornoxide prepared in Preparation Example 3 was used in place of the organic aluminum-t-butoxide prepared in Preparation Example 1, and the reaction was conducted. The reaction was stopped at the point at which the reacted amount of ethylene corresponded to the same reaction amount in Example 1 (the reaction time was 23 minutes), and the products were analyzed. The total yield was 3.56 g and the selectivity of hexene-1 was 76% by weight.

[0018]

Example 4

A catalyst was prepared in the same manner as in Example 1 except that 1.0 milliliter (1 millimole) of the cyclohexane solution of 1 mole/liter of TIBA was used in place of 1.5 milliliter of the cyclohexane solution in Example 1, and the reaction was conducted. The reaction was stopped after the elapse of 73 minutes, whereby 3.18 g of ethylene reaction products was obtained. The selectivity of each of the products was as follows. Hexene-1 was 78% by weight, octene-1 was 6% by weight, and polymers were 15% by weight.

[0019]

Example 5

A catalyst was prepared in the same manner as in Example 4 except that 10 milliliter (Al: 4.2 millimole) of the organic

aluminum-t-butoxide solution prepared in Preparation Example 1 was used in place of 20 milliliter of the organic aluminum-t-butoxide solution in Example 4, and the reaction was conducted. The reaction was stopped after the elapse of 202 minutes, whereby 2.78 g of ethylene reaction products was obtained. The selectivity of each of the products was as follows. Hexene-1 was 67% by weight, octene-1 was 4% by weight, and polymers were 27% by weight.

[0020]

Example 6

A catalyst was prepared in the same manner as in Example 4 except that 10 milliliter (Al: 4.2 millimole) of the organic aluminum-t-butoxide solution prepared in Preparation Example 1 was used in place of 20 milliliter of the organic aluminum-t-butoxide solution, and further that 10 milliliter (the electron donor: 0.5 milliliter) of the dimethoxyethane solution was used in place of 20 milliliter of the dimethoxyethane solution in Example 4, and the reaction was conducted. The reaction was stopped after the elapse of 68 minutes, whereby 2.89 g of ethylene reaction products was obtained. The selectivity of each of the products was as follows. Hexene-1 was 76% by weight, octene-1 was 5% by weight, and polymers were 17% by weight.

[0021]

Comparative example 1

A catalyst was prepared in the same manner as in Example 1 except that no organic aluminum-t-butoxide prepared in the

preparation example 1 was added, and the reaction was conducted. Even after the elapse of 120 minutes of the reaction time, no reaction consuming ethylene occurred.

[0022]

[Advantages of the Invention]

As compared with the case where oxygen-containing aluminum compounds obtained through hydrolysis with water, and the like are applied, selectivity of trimer or tetramer of ethylene, hexene-1, or octene-1 useful as a comonomer for linear low-density polyethylene (L-LDPE) can be improved in the manufacturing method of the present invention by using an aluminum alkoxide as a cocatalyst.